

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BR 00/00006

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C14C3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C14C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 41 02 545 A (BASF AG) 30 July 1992 (1992-07-30) column 1, line 30 -column 3, line 59 examples 1,4	1,2,5,6
A	DATABASE WPI Section Ch, Week 199843 Derwent Publications Ltd., London, GB; Class D18, AN 1998-496369 XP002135761 & BR 9 604 733 A (CHAHINE K I), 8 September 1998 (1998-09-08) abstract	1,3

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

14 April 2000

Date of mailing of the international search report

27/04/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5518 Patentaan 2
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/BR 00/00006

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 199220 Derwent Publications Ltd., London, GB; Class D18, AN 1992-165014 XP002135762 & SU 1 666 542 A (LEATHER SHOE IND RES INST), 30 July 1991 (1991-07-30) abstract	1,3,4
A	DE 44 30 290 A (BASF AG) 29 February 1996 (1996-02-29) page 2, line 28 -page 3, line 49 example 1	1,5,6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BR 00/00006

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4102545 A	30-07-1992	DE 59201788 D WO 9213105 A EP 0569410 A ES 2070632 T JP 6504800 T US 5372609 A	04-05-1995 06-08-1992 18-11-1993 01-06-1995 02-06-1994 13-12-1994
BR 9604733 A	08-09-1998	NONE	
SU 1666542 A	30-07-1991	NONE	
DE 4430290 A	29-02-1996	NONE	

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

PORTAL, Gérard et al.
CABINET BEAU DE LOMENIE
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RECU LE

24 JUL 2001

cabinet beau de lomenie

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 18.07.2001

Applicant's or agent's file reference
J32538-1WOGPO

IMPORTANT NOTIFICATION

International application No.
PCT/BR00/00006

International filing date (day/month/year)
02/02/2000

Priority date (day/month/year)
30/04/1999

Applicant
RHODIA BRASIL LTDA et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference J32538-1WOGPO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/BR00/00006	International filing date (day/month/year) 02/02/2000	Priority date (day/month/year) 30/04/1999
International Patent Classification (IPC) or national classification and IPC C14C3/08		
Applicant RHODIA BRASIL LTDA et al.		


1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☒ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 29/11/2000	Date of completion of this report 18.07.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Boonen, J Telephone No. +49 89 2399 8513



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/BR00/00006

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-3,5-10 as originally filed

4 as received on 21/05/2001 with letter of 18/05/2001

Claims, No.:

1-12 as received on 21/05/2001 with letter of 18/05/2001

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:
- ☐ the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/BR00/00006

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations
see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/BR00/00006

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. The present claims 1 to 12 are both novel and inventive as required by Article 33(2),(3) PCT.
Document D1 DE-A4 102 545 discloses the tanning of hydes using aldehydes as disclosed in examples 1 and 2.

The present claims 1 to 11 relate to a process for the tanning of hydes using alpha and beta hydroxy ketones of formulas I and II.

These ketones are less toxic while obtaining the same tanning quality.

The present claim 12 relates to skin or hide treated according to claims 1 to 11.

Re Item VII

1. The amended claims 1 to 12 fulfil the requirements of Article 34(b) PCT.

the tanning bath, by not containing salt, can be recycled after simple elimination of the fibers, through filtration.

The step of basification in the chrome tanning process can cause stains in the leather, in the case of quick additions of the basifying agent or larger doses than
5 necessary; it is, therefore, always a problematic stage, that should be made with care and attention.

The hides, after deliming, bating and the pre-treatment with the carbonyl compounds (I) and (II) described in this invention, propitiate a higher absorption of the chrome from the bath, dispense the previous use of the pickling stage and the
10 addition of the chrome salt can be made at a pH in the range of 4 to 6. After the normal chrome tanning time, the pH of the bath ends up at the range of 3.8 to 4.1; no correction of basicity is needed.

A larger exhaustion of the chrome bath is also described in the European patents EP 0 822 263 and Brazilian patents PI 96.3419-0 A and PI 9702025-7 A, by the use
15 of a water solution of stabilized aldehydes, more specifically, 3-hydroxyl butanal (aldol).

DE-A-402 545 discloses a process for tanning hides in which aldehydes are used.

However, aldehydes in general are extremely toxic and have a small limit of
20 exposition, as for example, 2-hydroxyl butanal (aldol), whose LD₅₀ is 2180 mg/kg (mice, oral) (Reference: H.E. Christensen, Toxic Substances, Edition 1974, p.166).

Aldol, particularly, frequently contains crotonaldehyde as an impurity (2-butenal), which is lacrimator, extremely irritant to the eyes (Reference: Merck Index 9th Edition, p. 338), with an extremely low exposition: TLV-TWA = 2 mg/kg
25 (Reference: Compendium of Safety Data Sheets for Research and Industrial Chemicals, p. 427).

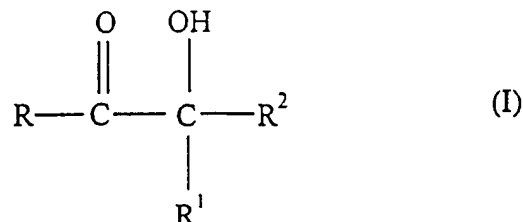
The aldol characteristics described previously make this product extremely difficult to be handled in the tanning plants. Besides this, the hides treated with aldol acquire an intense and suffocating residual odor.

30 The present invention describes the application of carbonyl compounds, such as hydroxy ketones and, preferentially, β -hydroxy ketones, where the hides, before the chrome tanning process or tanning process, with or without pickling, are pre-treated with the carbonyl product, at 0.1% to 30%, preferentially 0.5% to 10% and, better still, 1% to 5% of weight, in relation to the weight of the hides.

35 The hides, pre-treated with the carbonyl compounds of general structure (I) and (II), are prepared for the process to produce the "Wet Blue" leathers, and may also be

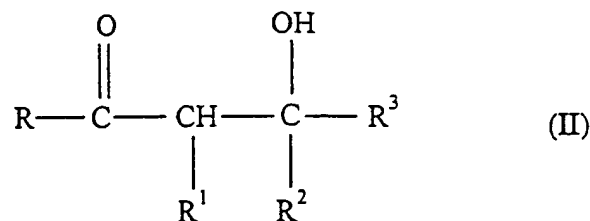
NEW SET OF CLAIMS

1. A process of tanning hide or skin characterized in that it comprises a step of contacting said skin or hide with α -hydroxy ketones of general formula (I)



wherein R^1 is a linear or ramified alkyl group or an aromatic group and R^1 and R^2 independently are hydrogen, a linear or ramified alkyl group or an aromatic group, and R^1 and R^2 are not concomitantly H.

or of contacting said hide or skin with β -hydroxy ketones of general formula (II)



wherein R is a linear or ramified alkyl group or an aromatic group and R^1 and R^2 and R^3 independently are hydrogen, a linear or ramified alkyl group or an aromatic group.

2. Process according to claim 1, characterized in that it comprises a step of contacting said skin or hide with the α -hydroxy ketones of formula (I).

3. Process according to claim 1, characterized in that it comprises a step of contacting said skin or hide with the α -hydroxy ketones of formula (I) wherein $\text{R} = \text{CH}_2\text{CH}_3$ or CH_3 and when $\text{R}^2 = \text{H}$, R^3 is an alkyl.

4. Process according to claim 1 or 2, characterized in that it comprises the step of contacting said skin or hide with the β -hydroxy ketones of general formula (II) wherein R is CH_3 , R^1 is H or CH_3 , R^2 is CH_3 , and R^3 is CH_3 or H.

5. Process according to anyone of claims 1, 2 or 4, characterized in that said β -hydroxy ketones is diacetone alcohol.

6. Process according to anyone of the preceding claims, characterized in that the amount of said α - or β -hydroxy ketones ranges from about 0.1% to 100% by weight based on the total weight of said skin or hide.

7. Process according to anyone of the preceding claims, characterized in that said α - or β -hydroxy ketones is used (a) as such, (b) diluted in water or (c) in mixtures with other organic compounds acting as diluents, with or without water.

8. Process according to anyone of the preceding claims, characterized in that:

- the concentration of said α - or β - hydroxy ketones ranges from about 0.1% to about 30% in weight based on the total weight of hide;

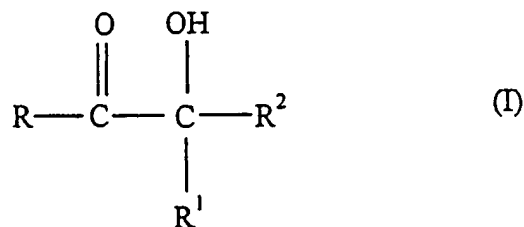
- said step of contacting skin or hide with said α - or β -hydroxy ketones precedes a step of contacting the skin or hide with a chrome salt or tannin.

9. Process according to claim 8, characterized in that said concentration of α - or β -hydroxy ketones ranges from about 0.5% to about 10% in weight based on the total weight of hide.

10. Process according to claim 8, characterized in that said concentration of α - or β -hydroxy ketones ranges from about 1% to about 5% in weight based on the total weight of hide.

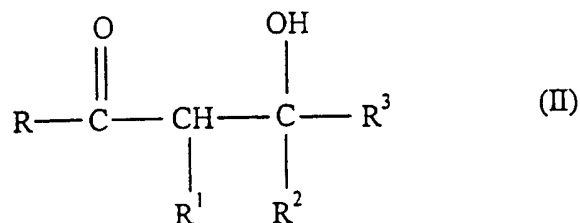
11. A process of tanning skin or hide, characterized in that it comprises some or all of the following steps:

- deliming;
- bating;
- pickling;
- conditioning with α -hydroxy ketones of formula I



wherein R¹ is a linear or ramified alkyl group or an aromatic group and R¹ and R² independently are hydrogen, a linear or ramified alkyl group or an aromatic group, and R¹ and R² are not concomitantly H,
or with β-hydroxy ketones of general formula (II)

5



- chromium or tannin tanning.

12. Skin or hide tanned by the process as claimed in anyone of the
10 preceding claims.